

IMPROVED MULTI-STAGE COUNTERCURRENT HYDROTREATING PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a continuation-in-part of Continued Prosecution Application 09/006,734 filed January 15, 1998, which was filed as a continuation-in-part of U.S.S.N. 08/702,334 filed August 23, 1996, now abandoned.

FIELD OF THE INVENTION

[0002] The present invention relates to a countercurrent process for removing heteroatoms, particularly organic sulfur and nitrogen components, from liquid petroleum and chemical streams. The feedstream flows countercurrent to the flow of a hydrogen-containing treat gas and is reacted with a first catalyst which is relatively tolerant to sulfur and nitrogen, such as a CoMo supported catalyst. When the level of organic sulfur in the feedstream is less than about 3,000 wppm and the level of organic nitrogen is less than about 1,000 wppm, the feedstream is reacted with said counter flowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and at least one Group VIA metal selected from Mo, W, or both, on a refractory support. The reaction vessel preferably contains vapor and optionally liquid by-pass means in one or more of the catalyst beds.

BACKGROUND OF THE INVENTION

[0003] There is a continuing need in the petroleum refining and chemical industries for improved catalyst and process technology. One type of process technology, which is often referred to as hydrotreating, involves the use of certain catalysts, typically those containing both Group VIA and Group VIII metals, for the removal of heteroatoms, such as sulfur, nitrogen, and sometimes oxygen. More active catalysts and improved reaction vessel designs are needed to meet this demand. Countercurrent reaction vessels have the potential of meeting some of this

[0004] While the concept of countercurrent hydroprocessing has been known for some time, countercurrent flow reaction vessels are typically not used in the petroleum industry primarily because, as previously mentioned, conventional countercurrent reaction vessels are susceptible to upset by catalyst bed flooding. While flooding is undesirable, catalyst contacting by the reactant liquid improves as the bed approaches flooding conditions. However, operating close to the point of incipient flooding leaves the process vulnerable to fluctuations in pressure or temperature or in liquid or gas flow rates. This could result in a disturbance large enough to initiate flooding and process unit shutdown, in order to recover stable operation. Such disruptions are highly undesirable in a continuous commercial operation.

[0005] Reaction vessels have been disclosed in U.S. Patent Nos. 5,705,052 and 5,720,872 both entitled "Countercurrent Reactor," and both of which are incorporated herein by reference. These applications disclose countercurrent reactors which are less susceptible to flooding than conventional countercurrent reaction vessels. This is primarily due to the novel use of vapor passageways, or

[0006] While the use of vapor by-pass means, typically tubes, has made the use of countercurrent reactors more commercially feasible, there is still a need in the art for improved catalyst staging in such vessels.

[0007] In accordance with the present invention, there is provided a multi-stage process for removing sulfur and nitrogen containing components from petroleum and chemical feedstreams containing at least one of said components, in the presence of a hydrogen-containing treat gas flowing countercurrent to the flow of said feedstream, the process which comprises:

reacting said feedstock in a first reaction stage with said hydrogen-containing treat gas in at least one catalyst zone containing a catalyst comprised of Co and Mo on a refractory support until the reacted feedstock contains less than about 3,000 wppm sulfur and less than about 1,000 wppm nitrogen; and

reacting said reacted feedstock in a second stage with counterflowing hydrogen-containing treat gas in the presence of at least one zone of catalyst comprised of Ni and a Group VIA metal selected from one or both of Mo and W, on a refractory support.

[0008] In one embodiment of the present invention, the reaction vessel contains a third reaction stage downstream of said second reaction stage, which third reaction stage is an aromatic hydrogenation stage or a hydrocracking stage.

[0009] In another preferred embodiment of the present invention, one or more of the reaction stages contains at least one vapor passageway extending through or around at least a portion of the catalyst bed of the stage containing the vapor

passageway so that a portion of upflowing hydrogen-containing treat gas can bypass a vertical portion of said catalyst bed.

[0010] In still another embodiment of the present invention, the feedstock is a distillate boiling range feedstock and is reacted in the presence of the Ni/Group VIA metal catalyst only when its sulfur level reaches less than about 1,500 wppm and its nitrogen level reaches less than about 750 wppm.

[0011] In yet another embodiment of the present invention, at least some of the vapor passageways are external to the reaction vessel.

BRIEF DESCRIPTION OF THE FIGURES

[0012] Figure 1 hereof is a reaction vessel of the present invention showing three reaction zones comprised of a catalyst bed, each of which contains vapor passageways so that upflowing vapor can bypass a reaction zone, and one liquid drain means.

[0013] Figure 2 is a representation of how the reaction vessel of Figure 1 will respond to a flooding situation while actions are taken to return bed hydrodynamics to normalcy.

[0014] Figure 3 is a plot of reactor residence time required to reach 10 ppm S as a function of percent CoMo/Al₂O₃ catalyst (Catalyst A - KF-757) in the first stage with the remaining catalyst being a NiMoW/Al₂O₃ (Catalyst B).

[0015] Figure 4 is a plot showing the required residence time to reach 10 ppm S as a function of where the interface between catalysts exists as indicated by S level.

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[0016] Feedstocks suitable for use in the practice of the present invention are those petroleum based feedstocks boiling in the distillate range and above. Such feedstocks typically have a boiling range from about 150°C to about 600°C, preferably from about 175°C to about 400°C. These feedstocks usually contain greater than about 3,000 wppm sulfur. Non-limiting examples of such feeds include virgin distillates, light cat cycle oils, light coker oils, vacuum gas oil (VGO), atmospheric gas oil (AGO), heavy atmospheric gas oil (HAGO), steam cracked gas oil (SCGO), deasphalted oil (DAO), and virgin and cracked distillates, and mixtures thereof.

[0017] Hydrotreating catalysts which are relatively tolerant to sulfur and nitrogen will be used in the first catalyst stage hereof. By "tolerant to sulfur and nitrogen" we mean catalysts that are not as easily poisoned by sulfur and nitrogen as is a NiMo-containing catalyst. Such sulfur/nitrogen tolerant catalysts will typically be those containing at least one Group VIII metal, preferably Fe or Co, more preferably Co; and at least one Group VIA metal, preferably Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. The Groups referred to herein are from the Period Table of the Elements, Sargent-Welch Scientific Co., 1980, Catalog No. S-18806. The Group VIII metal is typically present in an amount ranging from about 2 to 20 wt.%, preferably from about 4 to 12%. The Group VIA metal will typically be present in an amount ranging from about 5 to 50 wt.%, preferably from about 10 to 40 wt.%, and more preferably from about 20 to 30 wt.%. All metals weight percents are on support. By "on support" we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g. then 20 wt.% Group VIII metal would mean that 20 g. of Group VIII metal was on the support. It is within the scope of the present invention that more than one type of sulfur/nitrogen tolerant hydrotreating catalyst be used in this first reaction stage. For example, two or more

different hydrotreating catalysts can be blended together and used in a mixed catalyst bed. Further, two or more hydrotreating catalysts can be extruded together so that they are composited in the same extrudate. Also, two or more hydrotreating catalysts can be used in separate catalyst beds, preferably fixed beds, wherein each catalyst bed will represent a catalyst stage within the same single catalyst zone. That is, each catalyst zone can contain more than one catalyst stage. Typical hydrotreating temperatures will range from about 100°C to about 400°C at pressures from about 50 psig to about 2,000 psig. Liquid hourly space velocities are from about 0.2 to 10 volumes of liquid per volume of catalyst per hour. Typical treat gas rates are from about 200 to about 3,000 SCF hydrogen-rich gas per barrel of feedstock.

[0018] It has been found by the inventors hereof that a second stage is employed when the feedstream contains less than about 3,000 wppm, preferably less than about 1,500 wppm, and more preferably less than about 1,200 wppm sulfur; and less than about 1,000 wppm, preferably less than about 750 wppm, and more preferably less than about 500 wppm nitrogen. The catalyst of this second stage is comprised of Ni and one or both of Mo and W and is found to remove unexpectedly more of the remaining sulfur and nitrogen components when compared to other conventional hydrotreating catalyst. Non-limiting catalysts used in this second stage include NiMo, NiW, and NiMoW, on a refractory support. Preferred are NiMo and NiMoW, and more preferred is NiMoW. Thus, it is critical to the present invention that a second stage be employed where the feedstream contains the relatively low levels of sulfur and nitrogen components be subjected to a said Ni-based supported hydrotreating catalyst.

[0019] In conventional countercurrent processing, the vertically upflowing treat gas has the potential of hindering the downwardly flowing liquid feedstream to such a degree to cause reactor flooding. That is, by not allowing liquid to drain through the catalyst bed(s) in the reactor. At low liquid and gas velocities the

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hindrance from the slowly moving gas is not enough to cause flooding and the liquid in the reaction vessel is able to pass through the catalyst bed or beds. However, if either the upflowing gas rate or the downflowing liquid rate is high enough, liquid cannot drain through the catalyst bed. As the liquid holdup in a catalyst bed increases, liquid accumulates above the top surface of the bed. The upflowing gas rate at which flooding occurs in a given catalyst bed will depend on such things as the flow rate and the physical properties of the downflowing liquid. Similarly, the downflowing liquid flow rate at which flooding occurs in a given bed similarly depends on the rate and properties of upflowing gas.

[0020] The preferred countercurrent flow reaction vessels used in the practice of the present invention are less susceptible to flooding than conventional countercurrent reaction vessels because of vapor passageways which act to selectively bypass a fraction of the upward-moving treat gas so that it does not flow through one or more of the catalyst beds. The fraction of upflowing treat gas that bypasses a catalyst bed will increase as vapor pressure drop increases through a catalyst bed. Thus, the vapor passageways provide a self-adjusting regulation of upward-flowing vapor, thereby extending the hydrodynamic operating window of the reaction vessel. Further extension of this range can be provided by including one or more external vapor passageways having flow control means. Such a system provides a means by which catalyst bed pressure drop, and therefore catalyst contacting efficiency, can be controlled. Preferably, when both internal and external vapor passageways are provided, the external vapor passageways can be controlled with a control means, preferably a valve for so-called "trim" bypassing. The valve of course can be automatically operated so that it opens and closes to the appropriate degree in response to a signal transmitted relating to pressure drop changes in the catalyst bed(s). That is, the trim bypass will be used to keep the reaction vessel operating as close to flooding as desirable. The remaining treat gas stream, which does not bypass a particular catalyst bed or beds, will pass upward through the catalyst bed(s) and take part in the desired hydrotreating reaction, carry

away light or vaporized reaction products, and strip catalyst poisons such as hydrogen sulfide, water and/or ammonia, etc.

[0021] The vapor passageways of the preferred reaction vessels used in the practice of the present invention provide an extended operating range and an opportunity to operate close to the flooding point of the reaction vessel. This enables a more stable, more efficient reaction vessel operating regime. Further, the reaction vessel can safely and continuously operate while responding to normal process fluctuations in temperature and in liquid and vapor flow rate. The range of total flow rates that can be tolerated is thereby extended. Operating close to the flooding point results in very efficient contacting because the catalyst particles are well irrigated by the downflowing liquid. In the absence of vapor passageways, a conventional countercurrent reaction vessel would need to operate at lower efficiency in order to remain operable. The higher vapor flow rate capacity of the reaction vessels used in the practice of the present invention provides flexibility to use higher quench gas rates and/or treat gas rates, enabling a wider breadth of application for reactions involving high hydrogen consumption and heat release, such as aromatics saturation. Furthermore, the higher gas handling capacity enables the use of countercurrent reaction processing for reactions involving evolution of vapor phase products which might otherwise result in flooding due to excessive vapor generated during reaction, e.g., hydrocracking.

[0022] When flooding does occur, the reaction vessels used in the practice of the present invention are also more easily recovered and brought back to normal operation. During flooding, the liquid holdup in a catalyst bed increases and liquid may begin to accumulate above the top surface of the catalyst bed. This liquid must be drained to recover the reactor from a flooded state. The vapor passageways reduce gas flow rate through the catalyst bed(s), thus allowing the liquid to more easily drain through the catalyst bed(s). The liquid drain means of the present invention also helps recover the reaction vessel from flooding. Unless otherwise

stated herein, the terms "downstream" and "upstream" are with respect to the flow of liquid which will flow downward.

[0023] The preferred countercurrent flow reaction vessels used in the practice of the present invention can be better understood by a description of an example reaction vessel, which is shown in Figures 1 and 2 hereof. Miscellaneous reaction vessel internals, such as flow distributor means, thermocouples, heat transfer devices, etc., are not shown in the figures for simplicity. Figure 1 shows reaction vessel R which contains liquid inlet LI for receiving a feedstock to be treated, and a liquid outlet LO for removing liquid reaction product. There is also provided treat gas inlet GI and gas outlet GO. The reaction vessel contains three vertically disposed reaction zones, r_1 , r_2 , and r_3 . Each reaction zone is immediately preceded and immediately followed by a non-reaction zone, nr_1 , nr_2 , nr_3 , and nr_4 . The non-reaction zone may be a void, or empty section, in the reaction vessel. That is, a section which does not contain catalyst. Liquid distribution means LR (which is not shown in Figure 2 for simplicity) can be situated above each reaction zone in order to more evenly distribute downflowing liquid to the next downstream reaction zone. Each reaction zone is comprised of a bed of catalyst suitable for the desired reaction and each reaction zone can be a reaction stage or two or more reaction zones can comprise a reaction stage. One reaction stage can be distinguished from another reaction stage, for the purposes of this invention, by a change of catalyst. It is within the scope of this invention that one reaction zone can comprise more than one reaction stage. That is, a reaction zone can contain two different catalysts in a stacked bed arrangement. Also, the process conditions may be the same or different from one reaction stage to another.

[0024] Five vapor passageways VB_1 , VB_2 , VB_3 , VB_4 , and VB_5 and one liquid drain means LD are shown for the reaction vessels of the Figures, although any number and size of the vapor passageways can be used depending on the portion of the vapor one wishes to bypass the reaction zone(s). For purposes of the present

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invention, it is desirable that only a portion of the vapor bypasses one or more countercurrent reaction zones. It is preferred that less than about 50 vol.%, more preferably less than about 25 vol.%, and most preferably less than about 10 vol.% of the vapor bypasses any individual countercurrent reaction zone. The liquid drain means serves as a vapor passageway during normal operation but can allow liquid to drain during flooding upsets. It is to be understood that more than one liquid drain means can be used in any one or more reaction zones. The size and number of such liquid drain means will be dependent on such things as the size of the reaction vessel, the packing of the catalyst in the catalyst bed(s) and the flow rate of liquid feedstock through the catalyst bed.

[0025] The reaction vessel of Figure 1 is operated by introducing the feedstock to be treated into liquid inlet LI of reaction vessel R. A suitable treat gas, such as a hydrogen-containing gas, is introduced via port GI into the reaction vessel countercurrent to the downward flow of the liquid feedstock. The term "hydrogen-containing treat gas" means a treat gas stream containing at least an effective amount of hydrogen for the intended reaction. The treat gas stream will preferably contain at least about 50 vol.%, more preferably at least about 75 vol.% hydrogen. It is also preferred that the hydrogen-containing treat gas be make-up hydrogen-rich gas, preferably hydrogen. It is to be understood that the treat gas need not be introduced solely at the bottom of the reaction vessel at GI, but may also be introduced into any one or more of the non-reaction zones, for example at GI_a and/or GI_b. Treat gas can also be injected into any one or more of the catalyst beds. An advantage of introducing treat gas at various points in the reaction vessel is to control the temperature within the reaction vessel. For example, cold treat gas can be injected into the reaction vessel at various points to moderate any exothermic heat of reaction. It is also within the scope of this invention that all of the treat gas can be introduced at any one of the aforesaid points as long as at least a portion of it flows countercurrent to the flow of liquid in at least one reaction zone.

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[0026] The reaction vessels of the present invention are operated at suitable temperatures and pressures for hydrotreating reactions. The liquid feedstock passes downward through the catalyst bed of reaction zone r_1 , where it reacts with the treat gas on the catalyst surface. Any resulting vapor-phase reaction products are swept upwards by the upward-flowing treat gas. Such vapor-phase reaction products may include relatively low boiling hydrocarbons and heteroatom components, such as H_2S and NH_3 . Any unreacted feedstock, as well as liquid reaction product passes downwardly through each successive catalyst bed of each successive reaction zone r_2 and r_3 . Figure 1 shows an optional liquid distribution means LR which can be positioned above each catalyst bed. The ends of the vapor passageways may be situated above or below the liquid distribution means. For example, Figure 1 shows the upper end of vapor passageway VB_3 terminating at a point above liquid distribution means LR. The lower end of vapor passageways VB_1 and VB_2 terminate at a point below the liquid redistribution means LR. This arrangement allows selective bypassing of vapors produced in reaction zone r_2 to the reaction vessel gas outlet, while bringing a higher purity hydrogen-containing treat gas into catalyst bed r_1 by selectively bypassing higher-purity hydrogen-containing gas from r_3 to the inlet of catalyst bed r_1 . It is within the scope of this invention that the upper or lower ends of one or more of the vapor passageways terminate at a point within the reaction zone. The reaction vessel may employ any conventional distribution trays, such as sieve trays, bubble cap trays, etc. The liquid effluent exits the reaction vessel via port LO and vapor effluent via port GO. The preferred mode of operation of the reaction vessels of the present invention is to bypass only a portion of the vapor while still maintaining enough vapor upflowing through the catalyst bed(s) to meet the treat gas (hydrogen) demand for that catalyst bed(s) with relatively high kinetic efficiency.

[0027] As previously mentioned, countercurrent reaction vessels are typically susceptible to upset by flooding. That is, the upflowing treat gas can prevent liquid feedstock and liquid effluent from flowing downward through one or more catalyst

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beds. Figure 2 hereof depicts how the reaction vessel of Figure 1 would operate during a flooding situation to get the reaction vessel back on-stream without substantial downtime. For example, during a flooding situation in reaction zone r_2 , liquid holdup in the bed increases and liquid may begin to accumulate above the top surface of the catalyst bed. One or more liquid drain means LD are provided to allow the liquid to bypass one or more catalyst beds. Prior to flooding, the liquid drain means will act as a vapor passageway. The top of the liquid drain means can be flush with, or any height above the top surface of the catalyst bed. It is preferred that the top of the liquid drain means be substantially flush with the top surface of the catalyst bed. Any liquid that passes through the drain means can be passed to the next downstream bed or it can preferably be recycled to any one or more reaction zones.

[0028] The vapor and liquid drain passageways may be any suitable structure constructed from a material that can withstand the operating conditions of the reaction vessel. Suitable materials include metals, such as stainless and carbon steels; ceramic materials; as well as high performance composite materials such as carbon fiber materials. Preferred are tubular passageways. The passageways need not be perfectly vertical. That is, they can be inclined or curved, or even in the form of a spiral. They can also be perforated along the sides. It is to be understood that the passageways can be of any suitable size depending on the amount and rate of vapor one wishes to pass from one non-reaction zone to another. Further, one or more of the passageways, or drain means, can have a flat substantially horizontal member, such as a baffle, above it to prevent liquid from an upstream bed from falling into the passageways. Also, more than one passageway can be extended through at least a portion of any one or more reaction zones. It is preferred that the vapor passageways be extended entirely through the one or more reaction zones. When a plurality is used it is preferred that they be concentrically located about the vertical axis of the reaction vessel. One or more vapor passageways can also be routed external to the reaction zone. For example, a tubular arrangement can be

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used on the outside of the reaction vessel so that one or more non-reaction zones are in fluid communication with any one or more other non-reaction zones. The vapor passageways may contain a flow control means to control the portion of vapors which is passed from one non-reaction zone to another non-reaction zone. If the vapor passageways are external to the reaction vessel, then it is preferred that the flow control means be simply a flow control valve.

[0029] It is within the scope of the present invention that the vapor passageways bypass two or more catalyst beds, or reaction zones. Further, the vapor passageways need not be hollow structures, such as solid-walled tubes, but they may contain a packing material, such as inert balls. The packing material in the vapor passageways can be of a different size than the catalyst particles in the catalyst beds of the reaction zones. Such packing may help to improve the bypassing characteristics of said tubes. It is preferred that one or more co-current reaction zones be upstream of one or more countercurrent reaction zones. The zones can be in separate vessels or two or more zones can be in the same vessel. It is preferred that all countercurrent zones be in the same vessel.

[0030] In the case where the first reaction zone is a co-current hydrotreating reaction zone, the liquid effluent from said hydrotreating reaction zone will be passed to at least one downstream reaction zone where the liquid is passed through a bed of catalyst countercurrent to the flow of upflowing hydrogen-containing treat-gas. Depending on the nature of the feedstock and the desired level of upgrading, more than one reaction zone may be needed. For example, the first stage containing the sulfur/nitrogen tolerant catalyst can consist of two catalyst zones. The first catalyst zone of the first stage can be a co-current catalyst zone and the second a countercurrent catalyst zone.

[0031] The liquid phase in the reaction vessels of the present invention will typically be comprised of the higher boiling point components of the feed. The vapor phase will typically be a mixture of hydrogen-containing treat gas,

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heteroatom impurities, and vaporized lower-boiling components of the fresh feed, as well as light products of hydroprocessing reactions. The vapor phase in the catalyst bed of a countercurrent reaction zone will be swept upward with the upflowing hydrogen-containing treat gas and collected, fractionated, or passed along for further processing. If the vapor phase effluent still contains an undesirable level of heteroatoms and/or aromatics, it can be passed to a vapor phase reaction zone containing additional hydrotreating catalyst and subjected to suitable hydrotreating conditions for further removal of heteroatoms. It is to be understood that all reaction zones can either be in the same vessel separated by non-reaction zones, or any can be in separate vessels. The non-reaction zones in the later case, will include the transfer lines leading from one vessel to another.

[0032] In an embodiment of the present invention, the feedstock can be introduced into a first catalyst zone co-current with the flow of hydrogen-containing treat-gas and reacted with a sulfur/nitrogen tolerant catalyst. A vapor phase effluent fraction can then be separated from the liquid phase effluent fraction between reaction zones. That is, in a non-reaction zone. The vapor phase effluent can be passed to additional hydrotreating, or collected, or further fractionated. The liquid phase effluent will then be passed to the next downstream reaction zone, which will preferably be a countercurrent reaction zone. If the sulfur and nitrogen levels are below the 3,000/1,000 wppm levels respectively, this countercurrent zone can in fact be the second reaction stage containing the NiMo, NiW, or NiMoW catalyst instead of the more sulfur tolerant catalysts. If the levels of sulfur and nitrogen are still too high, then this countercurrent zone can contain another sulfur/nitrogen tolerant hydrotreating catalyst. In other embodiments of the present invention, vapor phase effluent and/or treat gas can be withdrawn or injected between any reaction zones.

[0033] The countercurrent contacting of liquid from an upstream reaction zone with upflowing treat gas strips dissolved H_2S and NH_3 impurities from the effluent

stream, and results in greater hydrogen partial pressure and improved catalyst performance downstream. The resulting final liquid product will contain a substantially lower level of heteroatoms and somewhat more hydrogen content than the original feedstock. This liquid product stream may be sent to downstream hydroprocessing or conversion processes.

[0034] It is within the scope of the present invention that additional reaction stages can follow the second reaction stage containing the Ni/Group VIA metal catalyst. One such stage can be an aromatics hydrogenation stage containing a noble metal sulfur sensitive hydrogenation catalyst. Non-limiting examples of noble metal catalysts include those based on platinum and/or palladium, which is preferably supported on a suitable support material, typically a refractory oxide material such as alumina, silica, alumina-silica, kieselguhr, diatomaceous earth, magnesia, and zirconia. Zeolitic supports can also be used. Such catalysts are typically susceptible to sulfur and nitrogen poisoning. The aromatic saturation zone is preferably operated at a temperature from about 40°C to about 400°C, more preferably from about 260°C to about 350°C, at a pressure from about 100 psig to about 3,000 psig, preferably from about 200 psig to about 1,200 psig, and at a liquid hourly space velocity (LHSV) of from about 0.3 V/V/Hr. to about 2.0 V/V/Hr.

[0035] A hydrocracking reaction stage can also be present downstream of the NiMo reaction stage. If one of the downstream reaction zones is a hydrocracking zone, the catalyst can be any suitable conventional hydrocracking catalyst run at typical hydrocracking conditions. Typical hydrocracking catalysts are described in U.S. Patent No. 4,921,595 to UOP, which is incorporated herein by reference. Such catalysts are typically comprised of a Group VIII metal hydrogenating component on a zeolite cracking base. The zeolite cracking bases are sometimes referred to in the art as molecular sieves, and are generally composed of silica, alumina, and one or more exchangeable cations such as sodium, magnesium,

calcium, rare earth metals, etc. They are further characterized by crystal pores of relatively uniform diameter between about 4 and 12 Angstroms. It is preferred to use zeolites having a relatively high silica/alumina mole ratio greater than about 3, preferably greater than about 6. Suitable zeolites found in nature include mordenite, clinoptilolite, ferrierite, dachiardite, chabazite, erionite, and faujasite. Suitable synthetic zeolites include the Beta, X, Y, and L crystal types, e.g., synthetic faujasite, mordenite, ZSM-5, MCM-22 and the larger pore varieties of the ZSM and MCM series. A particularly preferred zeolite is any member of the faujasite family, see Tracy et al., Proc. of the Royal Soc., 1996, Vol. 452, p. 813. It is to be understood that these zeolites may include demetallated zeolites which are understood to include significant pore volume in the mesopore range, i.e., 20 to 500 Angstroms. Non-limiting examples of Group VIII metals which may be used on the hydrocracking catalysts include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Preferred are platinum and palladium, with platinum being more preferred. The amount of Group VIII metal will range from about 0.05 wt.% to 30 wt.%, based on the total weight of the catalyst. If the metal is a Group VIII noble metal, it is preferred to use about 0.05 to about 2 wt.%. Hydrocracking conditions include temperatures from about 200°C to 425°C, preferably from about 220°C to 330°C, more preferably from about 245°C to 315°C; pressure of about 200 psig to about 3,000 psig; and liquid hourly space velocity from about 0.5 to 10 V/V/Hr, preferably from about 1 to 5 V/V/Hr.

[0036] The following examples are presented for illustrative purposes only and are not to be taken as limiting the present invention in any way.

EXAMPLES

Comparative Example A

[0037] A distillate containing a significant proportion of cracked stock was hydrotreated over a CoMo/Al₂O₃ catalyst (Akzo Nobel's KF-757) at conditions of

650 psig total pressure, 650°F (343°C), 1 liquid hourly space velocity (LHSV), and 2000 standard cubic feet per barrel SCF/B pure hydrogen treat gas co-current to the liquid flow to conduct desulfurization. The feedstock contained a sulfur level of 17200 wppm and a nitrogen level of 373 wppm. The product from such hydrotreating contained 37 wppm S and 10 wppm N. Brief space velocity scoping and a least squares regression of the data showed a power model reaction order of about 1.348 in total sulfur concentration and a rate constant of 0.25111 for this catalyst.

Comparative Example B

[0038] Comparative Example A was followed except a NiMoW/Al₂O₃ catalyst was used in place of the CoMo/Al₂O₃ catalyst. The metal component of the NiMoW/Al₂O₃ catalyst, on a metal oxide basis, was comprised of about 40 wt.% nickel oxide, about 40 wt.% molybdenum oxide, and about 20 wt.% tungsten oxide. There was also a small amount of binder present as well. The product from this hydrotreating contained 14 wppm S and <1 wppm N. Brief space velocity scoping and a least squares regression of the data showed a power model reaction order of about 1.0918 in total sulfur concentration and a rate constant of 0.3768 for this catalyst.

Example 1

[0039] Using the kinetics of each catalyst system, a mathematical simulation of a staged catalyst bed was conducted whereupon the relative amounts of two stages were adjusted to minimize sulfur content in the total product. The optimum staging was obtained by first treating the feed with the CoMo/Al₂O₃ catalyst located in the first 24.2 vol.% of the reactor bed followed by treating over the NiMoW/Al₂O₃ catalyst located in the remaining 75.8 vol.% of the reactor bed. By treating the feed in the sequence indicated for the time periods indicated (an effective residence time of 0.242 hours over the CoMo/Al₂O₃ catalyst followed by 0.758 hours over the NiMoW/Al₂O₃), a sulfur level of 8.6 wppm was achieved leaving the second stage.

The sulfur level at the interface between the stages was kinetically estimated to be 886 wppm. The total residence time was 0.758 hr + 0.242 hr for a total of 1 hr.

[0040] To achieve 8.6 wppm S at these conditions, but in a single stage at 1 LHSV, the CoMo/Al₂O₃ catalyst would have to be about 1.76 times more active. Similarly, to achieve 8.6 wppm S, using only the NiMoW/Al₂O₃ catalyst at 1 LHSV, the NiMoW/Al₂O₃ catalyst would have to be about 10% more active. It can thus be seen that the combination of the two stages, when properly performed, unexpectedly results in superior performance than would be indicated by the performance of either stage alone.

Comparative Example C

[0041] To illustrate kinetically the disadvantage of improper staging, the above system was reversed, i.e., the NiMoW/Al₂O₃ catalyst was located in the first 24.2 vol.% of the catalyst bed followed by the CoMo/Al₂O₃ catalyst in the remaining 75.8 vol.% of the bed. The resulting mathematical simulation showed that a sulfur level of 46.7 wppm would leave the second stage as compared with 8.5 wppm S in the optimized case. A single stage reactor containing the NiMoW/Al₂O₃ catalyst at 1 LHSV would have to be about 78% as active as itself to achieve 46.7 wppm. Stated another way, a CoMo/Al₂O₃ catalyst bed operating at 1.0 LHSV would have to be only about 91% as active as itself to achieve 46.7 wppm S. Thus, improper staging results in lower hydrodesulfurization activity.

Comparative Example D

[0042] A distillate containing a significant proportion of cracked stock was hydrotreated over a state-of-the-art CoMo/Al₂O₃ catalyst (Akzo Nobel's KF-757) at conditions of 650 psig total pressure, 650°F (343°C), 2.7 LHSV, and 2000 SCF/B pure hydrogen treat gas co-current to the liquid flow to conduct desulfurization. The feedstock contained a sulfur level of 17200 wppm and a nitrogen level of 373 wppm. The product from such hydrotreating contained 380 wppm S and 110 wppm

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N. Brief space velocity scoping and a least squares regression of the data showed a power model reaction order of about 1.348 in total sulfur concentration and a rate constant of 0.25111 for the CoMo/Al₂O₃ catalyst.

Comparative Example E

[0043] Comparative Example D was followed except the NiMoW/Al₂O₃ catalyst was used instead of the CoMo/Al₂O₃ catalyst. The product from this hydrotreating contained 700 wppm S and 52 wppm N. Brief space velocity scoping and a least squares regression of the data showed a power model reaction order of about 1.0918 in total sulfur concentration and a rate constant of 0.3768 for this catalyst. The kinetics are the same as quoted in Example 1.

Example 2

[0044] Using the kinetics of each catalyst system, a mathematical simulation of a staged bed was conducted whereupon the relative amounts of two stages were adjusted to minimize sulfur content in the total product. The optimum staging was obtained by first treating the feed with the CoMo/Al₂O₃ catalyst located in the first 65.3 vol.% of the reactor bed followed by treating over the NiMoW/Al₂O₃ catalyst located in the remaining 34.7 vol.% of the reactor bed. By treating the feed in the sequence indicated for the time periods indicated (an effective residence time of 0.242 hours over the CoMo/Al₂O₃ catalyst followed by 0.1285 hours over the NiMoW/Al₂O₃ catalyst) a sulfur level of 345.3 wppm was achieved leaving the second stage. The sulfur level at the interface between the stages was kinetically estimated to be 886 wppm as in Example 1 above.

[0045] To achieve 345.3 wppm S at these conditions but in a single stage at 2.7 LHSV, the CoMo/Al₂O₃ catalyst would have had to be about 5% more active. Similarly, to achieve 345.3 wppm S using only the NiMoW/Al₂O₃ catalyst at 2.7 LHSV would have required about 26% more activity out of the NiMoW/Al₂O₃

catalyst. It is thus confirmed that superior performance results from combining the two stages in a proper order and proportion.

Comparative Example F

[0046] To illustrate kinetically the disadvantage of improper staging, the above system was reversed, i.e. the NiMoW/Al₂O₃ catalyst was located in the first 65.3 vol.% of the catalyst bed followed by the CoMo/Al₂O₃ catalyst in the remaining 34.7 vol.% of the bed. The resulting mathematical simulation showed that a sulfur level of 662 wppm would leave the second stage as compared with 345.3 wppm S in the optimized case. A single stage reactor containing the NiMoW/Al₂O₃ catalyst would only have to be about 2% more active achieve 662 wppm. Similarly, to achieve 662 wppm S using only the CoMo/Al₂O₃ catalyst at 2.7 LHSV would have required activity only 76% of the CoMo/Al₂O₃ catalyst.

Example 3

[0047] In a further embodiment of the above invention, one can minimize reactor volume (residence time) needed to achieve a given sulfur target if the reactor is appropriately staged. For example, at the above temperature, treat gas rate and pressure, residence time to achieve 10 wppm S is minimized when approximately the first quarter of the reactor bed contains the CoMo/Al₂O₃ catalyst. This is shown in Figure 3. The residence time requirements can also be plotted against the sulfur level at the interface between the stages (Figure 4). This shows that the most advantageous time to switch from a CoMo-based to a NiMoW-based catalyst system is when the interstage sulfur levels reach a level of approximately 500-1500 wppm, or, more preferably, about 600-1000 wppm S.

**EFFECT OF CATALYST STAGING ON HETEROATOM REMOVAL
WITH DISTILLATE FEEDSTOCK CONTAINING 17,200 ppm S, and 373 ppm N**

Example	1st Stage Catalyst	LHSV	2nd Stage Catalyst	LHSV	Product S (ppm)	Product N (ppm)
Comp. A	CoMo/Al ₂ O ₃	1	No 2nd Stage		37	10
Comp. B	NiMoW/Al ₂ O ₃	1	No 2nd Stage		14	<1
1	CoMo/Al ₂ O ₃	1	NiMoW/Al ₂ O ₃	1	8.6	nil
Comp. C	NiMoW/Al ₂ O ₃	1	CoMo/Al ₂ O ₃	1	46.7	
Comp. D	CoMo/Al ₂ O ₃	2.7	No 2nd Stage		380	110
Comp. E	NiMoW/Al ₂ O ₃	2.7	No 2nd Stage		700	52
2	CoMo/Al ₂ O ₃	2.7	NiMoW/Al ₂ O ₃	2.7	345.3	nil
Comp. F	NiMoW/Al ₂ O ₃	2.7	CoMo/Al ₂ O ₃	2.7	662	

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